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Normal and *abnormal* carbene complexes derived from thiazole: Preparation and a preliminary investigation of their relative catalytic performance

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Readily prepared 2-, 4- and 5-bromo-3-methyl thiazolium triflates react by oxidative substitution with $M(PPh_3)_4$ (M = Ni or Pd) to furnish five of the expected *normal* and *abnormal* cationic thiazolylidene complexes (**1a**, **1b**, **2a**, **2b**, and **3b**). Carbene complex formation is accompanied by a ca. 40 ppm downfield shift of the α-N carbene carbons in Pd complexes **1** and **2** in their ^{13}C NMR spectra but the chemical shift of C(carbene) in the *abnormal* **3b** (δ 135.7) is particularly low. Crystal and molecular structures of complexes **1a**, **2b**, and **3b** all indicate a square planar arrangement of the ligands around the central metal atoms. The new complexes catalyse Suzuki–Miyaura aryl coupling.

1. Introduction

Despite the fact that free thiazolylidenes have not yet been isolated [1], nature has been using them since the beginning of advanced life as has been shown by Breslow in the context of ylidene catalysed benzoin condensations [2]. The first preparations of NHC complexes wherein the heterocyclic ring also contains an S atom, have been independently carried out by Lappert [3] and Stone [4,5] using different synthetic approaches. Fehlhammer and co-workers [6] have used the addition of CS_2 to metal-coordinated α-deprotonated ethyl isocyanoacetate to form such carbene complexes of chromium and tungsten and, subsequently, a palladium complex by ligand transfer and substitution.

We entered the field in the early nineties [7], when reporting thiazolylidene complexes of gold. By removing the relative acidic proton in the 2-position of the parent thiazole with BuLi, an active anionic precursor ligand was generated. Carbene complexes were easily realised by successive transmetallation and protonation or alkylation [8]. Later, Nacci and co-workers [9] synthesised benzothiazolylidene complexes of PdI_2 which catalysed the Heck reaction [10]. Such catalytic activity was shown to be enhanced by modifications to the ligands and complexes [11].

In all the publications referred to above, so called *normal* thiazolylidene complexes have been used. This description refers to the fact that the metal is bonded in the 2-position of this chosen heterocyclic ring and, hence, that a Lewis structure can be written for the complexes without the necessity of invoking any formal charge on the ligand (compare contributing structure iii in Scheme 1) [12].

Various examples of *abnormal* or *mesoionic* NHC complexes are now known with most of them belonging to the imidazolylidene or pyridylidene families [13]. In the former examples, the metal is bonded in the 4-position of the heterocyclic ring (Fig. 1) and no simple neutral resonance structure for the ligand can be drawn. π-Backdonation, to the ring is still possible in principle and can best be understood in terms of an MO approach. Consensus has been reached that, in general, very little M → L π-backdonation occurs in known *abnormal* carbene complexes [13]. In most publications the metal–ligand bond in both *normal* and *abnormal* azolylidene or pyridylidene complexes is represented by a single line. The double bond description is used either to indicate carbene ligands as such, when back-donation is invoked, or when the relative importance of various structures is discussed [12,13].

Three carbene types can in principle be derived from thiazolium salts, one *normal* and two *abnormal*, depending on the relative

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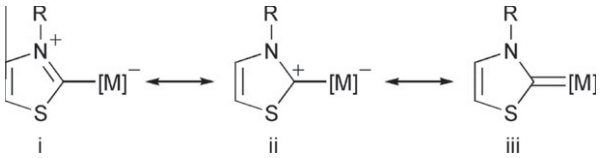


Scheme 1.

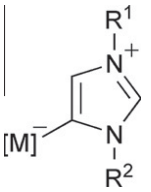


Fig. 1. *Abnormal* imidazolylidene complex.

position of the carbene carbon with respect to the two heteroatoms (Fig. 2 with formal charges omitted).

Below, the preparation of examples of all three complex types via oxidative addition [14] is described as well as a preliminary comparative study of the catalytic activity of their palladium complexes in simple Suzuki–Miyaura coupling reactions.

2. Results and discussion

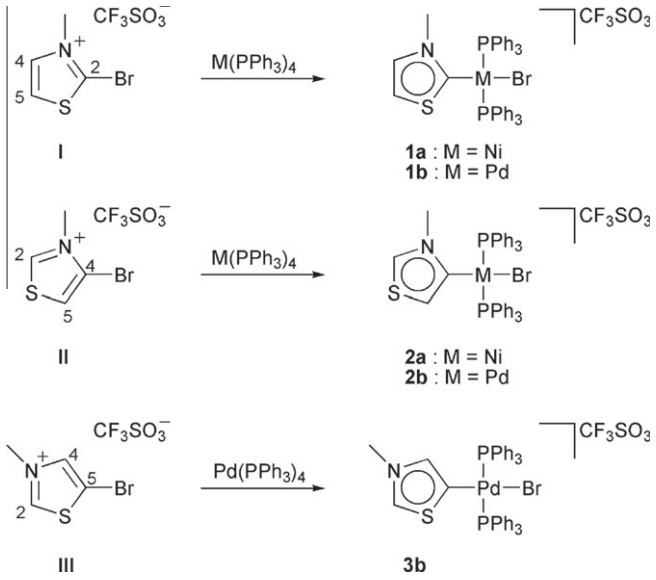
2.1. Synthesis

The colourless 2-, 4- and 5-bromo-3-methyl thiazolium triflate salts (**I**–**III**) were prepared in high yields by alkylation of the corresponding neutral bromo thiazoles with methyl triflate. Reaction of these salts with $M(PPh_3)_4$ (M = Ni or Pd) afforded by oxidative substitution in THF (**1a**, **1b**, **2a**) or toluene (**2b**, **3b**) solution, the complexes **1**–**3** in Scheme 2. Unexpectedly, complex **1b** was obtained in only 8% yield (none in toluene) whilst the other palladium compounds, **2b** and **3b**, formed in high yields, all as colourless, microcrystalline material. Moderate (36.3% and 45.9%) yields of the two yellow nickel products **1a** and **2a** were isolated. The nickel analogue of **3b** could not be isolated.

2.2. Characterisation

All the product complexes display a single signal in their ^{31}P NMR spectra indicating the presence of two *trans*-orientated phosphine groups. Phenyl protons and carbon atoms of these ligands resonate in the same region as previously found for related pyridylidene complexes [15]. Assignments are reported in Section 4. In both the complexes **1a** and **1b** and their thiazolium precursor **I** (as well as in unbrominated thiazolium salts [15]) the ^{13}C chemical shifts of the carbon atoms in position 2 are the most downfield followed by those of 4-C and 5-C. When 4-C becomes a carbene donor atom (in **2a** and **2b**), its ^{13}C chemical shift is also observed the most downfield of the concerned ring carbons. The value for 5-C in the *abnormal*(S) carbene complex **3b**, however, remains the lowest of the three ring carbons in this particular ligand experiencing only a rather small 20 ppm downfield shift upon carbene complex formation from the brominated thiazolium salt **III**.

Although the normal complexes **1a** and **1b** exhibit the highest (δ 200.9 and δ 197.8) chemical shifts for their respective carbene carbon atoms, the corresponding resonances for **2a** and **2b** (δ 163.6 and δ 165.1) are also found ca. 40 ppm downfield from the 4-C chemical shift in the precursor immonium salt **II**. The δ



Scheme 2.

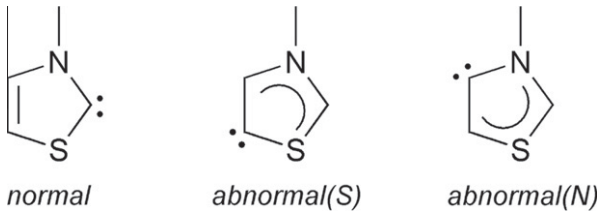


Fig. 2. Various free thiazolylidenes.

135.7 chemical shift of the metal-bonded carbon atom in **3b** is remarkably low compared to that (δ 189.9) of a known α-S carbene complex of iron derived from an isothiazolium salt in which the nitrogen atom is also placed in a *remote* (but *normal*) position [16]. The cations of the new ligand precursors **I**–**III** are observed in their EI mass spectra. The presence of various isotopic mixtures of the metals and bromine are indicated by the FAB mass spectra of the complexes. For compounds **1a**, **2a**, **2b** and **3b** all the cationic coordination complex ions are clearly shown followed by the successive loss of a PPh_3 ligand and Br. For **1b** the fragment $Pd(PPh_3)_2^+$ is detected.

2.3. Molecular structures of *1a*, *2b* and *3b*

The crystal and molecular structures of compounds **1a**·CH_2Cl_2, **2b**, and **3b**·CH_2Cl_2 were determined by X-ray diffraction. Compounds **1a** and **3b** each crystallise as solvates with one molecule of dichloromethane per formula unit, while **2b** forms solvent free crystals with two sets of independent molecules in the asymmetric unit. The bond lengths and angles in these two molecules do not differ significantly from each other.

To the best of our knowledge, these structures represent the first examples of thiazolylidene ligands bound to group 10 metals. Further, the *abnormal* bonding featured in the palladium complexes of **2b** and **3b** is unprecedented with any metal. The adopted numbering schemes are shown in Figs. 3–5. Selected bond lengths and angles are given in Table 1.

All cationic complexes present in the crystals of **1a**, **2b**, and **3b** exhibit the now already familiar geometry established for related, phosphine-containing group 10 NHC complexes [17,18]. All the do-

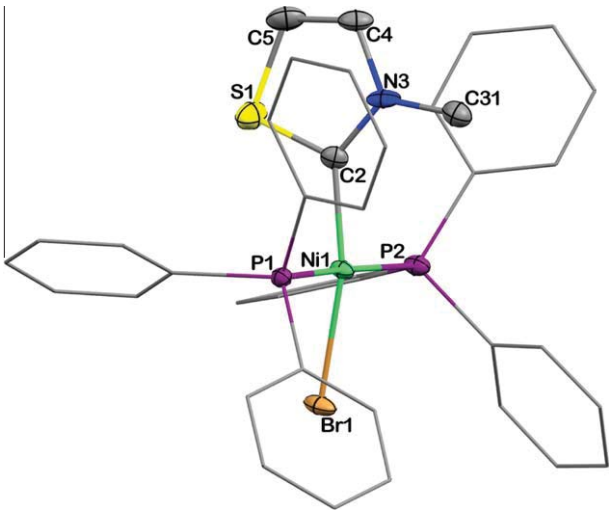


Fig. 3. Molecular structure of the cationic complex **1a** (50% probability ellipsoids, hydrogen atoms, counter ion and solvent omitted).

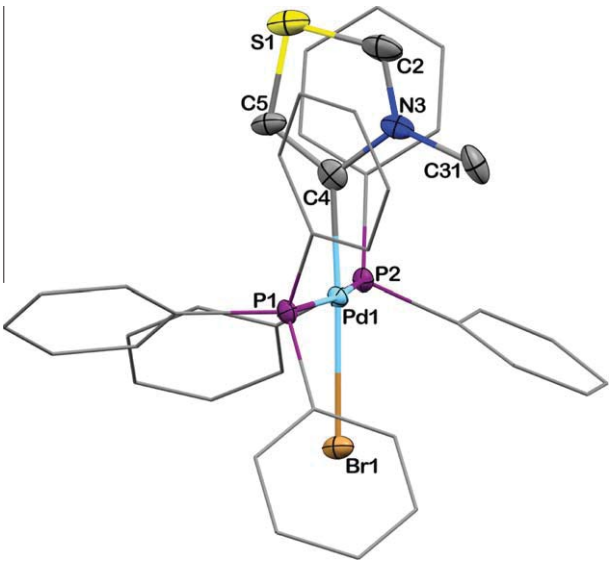


Fig. 4. Representative molecular structure of the cationic complex **2b** (50% probability ellipsoids, hydrogen atoms, counter ions and second independent molecule omitted).

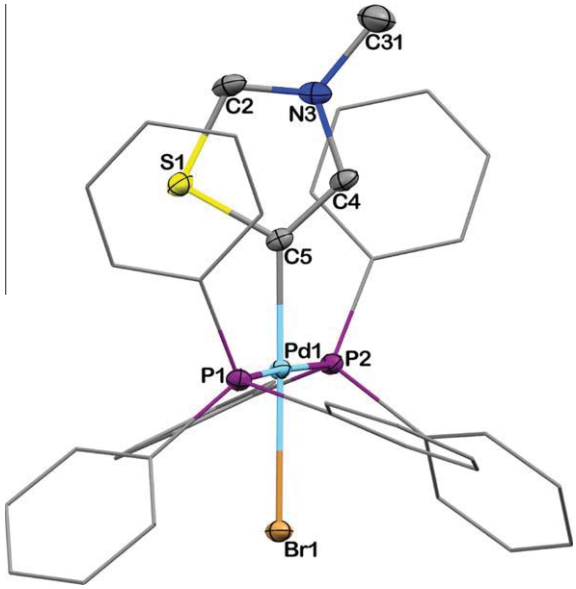


Fig. 5. Molecular structure of the cationic complex **3b** (50% probability ellipsoids, hydrogen atoms, counter ion and solvent omitted).

nor atoms are arranged in a square plane around the metal with the phosphine ligands mutually *trans* oriented. Notably, only the normal nickel complex **1a** shows significant distortion of the coordination plane. The essentially flat heterocyclic ligands adopt a largely perpendicular orientation to this coordination plane (**1a**: 89°; **2b**: 87°, 84°; **3b**: 77°). The deviation of ca. 13° observed for **3b** is rather large and can be understood by the absence of *ortho* substituents in the carbene ligand in **3**, thus contrasting the carbenes in **1** and **2**.

Structural data for unsubstituted thiazolium salts within their rings [19,20] indicate that the S–C2–N angle is wider than the S–C5–C4 angle. The *normal* thiazolylidene complex features, however, the smallest angle at the metal bound C2-atom. The compression of the S–C2–N bond angle upon metallation is accompanied by a distinct elongation of the C2–S1 and, to a slighter extent, of the C2–N3 bond. Identical modifications have been noted when comparing the more abundant structural data of benzothiazolium salts with benzothiazolylidene nickel and palladium complexes [21].

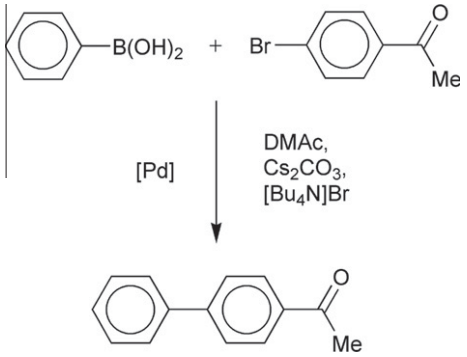
All known 2-thiazolylidene metal complexes, (M = Cu, Mo, Au, Mn) show the mentioned compression of the S1–C2–N3 angle upon exchange of a proton in the thiazolium salt for a metal fragment. This effect seems to be universal, since other substituents (e.g. ethyl, NH_2) than metal units have the same effect. The S1–C2 bond distance is, however, not always lengthened. This second, independent effect could offer a measure for the backbonding ability of the C2-substituent or metal fragment, since NH_2 does show elongation and Et not. However, further systematic studies need to be conducted to support such a notion. We conclude already that the S1–C2 bond seems to be much more sensitive than the N3–C2 bond for detecting changes at C2 *reflected in Table 1* and thus also its participation in carbene complex stabilisation.

In the *abnormal* complexes **2b** and **3b**, no significant effects on the bond lengths involving the carbene carbons can be observed after substitution of a proton by a metal fragment. It is, however, again at this carbon where the most compressed angle is found in both complexes. This result is similar to the observations made above and also holds if the metal fragments are replaced by alkyl or amino substituents. It is known that the N–C–N angle in imidazolium salts decreases significantly upon free carbene formation by deprotonation [22] – probably owing to more π-character in the surrounding bonds following Bent's rule [23]. We established that complexation (or other formal addition of cationic fragments) does not allow the ring to revert back completely to its electronic situation in the azolium salt.

The bond lengths within the heterocyclic rings of all three compounds indicate that the original bonds in the precursor thiazolium salts remain largely intact and thus that the formal positive charge on the nitrogen atom of each ligand is retained indicating that essentially zwitterionic ligands are bonded to the metals (compare contributing structure i in Scheme 1 showing such a ligand coordinated to a metal fragment [M]). The metal–carbon separations in **1a** [1.858(6) Å], **2b** [1.995(7) Å, 2.002(7) Å] and **3b**: [1.987(4) Å] compare well with other pyridylidene [18,24] and *abnormal* imidazolylidene [25,26] complexes of Ni(II) and Pd(II), respectively. The Ni–P and Pd–P bonds are longer than the corresponding bonds in similar imidazol-2-ylidene [18,27] complexes but do not differ significantly from the same bonds in pyridylidene [15] and thiazol-2-ylidene [28] and isoquinolylidene (Pd only) complexes [29].

Table 1
Selected bond distances of **1a**, **2b** and **3b**.

	1a	2b	3b
Bond lengths (Å)			
M–C	1.858(6)	1.995(7)	1.988(4)
M–Br	2.3099(9)	2.4743(9)	2.4750(5)
M–P1	2.2263(16)	2.3233(17)	2.3278(11)
M–P2	2.2231(16)	2.3187(17)	2.3325(11)
S1–C2	1.713(6)	1.666(9)	1.684(4)
C2–N3	1.348(8)	1.306(9)	1.314(6)
N3–C4	1.401(8)	1.402(9)	1.397(5)
C4–C5	1.317(9)	1.355(10)	1.343(6)
C5–S1	1.730(7)	1.709(7)	1.737(4)
N3–C31			
Bond angles (°)			
C–M–Br	163.96(18)	176.9(2)	179.32(12)
P1–M–P2	173.02(7)	169.36(6)	175.66(4)
S1–C2–N3	109.9(4)	112.8(6)	111.5(3)
C2–N3–C4	113.9(5)	115.4(7)	113.5(4)
N3–C4–C5	113.6(6)	108.2(7)	114.2(4)
C4–C5–S1	110.7(5)	113.4(6)	108.2(3)
C5–S1–C2	91.9(3)	90.1(4)	92.6(2)



Scheme 3.

The Ni–Br bond length of 2.3099(9) Å in **1a** is significantly shorter than in other *normal* 2-imidazolylidene nickel complexes [30,31]. The two rather similar Pd–Br bond distances in the *abnormal*(N) and *abnormal*(S) thiazolylidene complexes **2b** and **3b** (ca. 2.47 Å) are significantly shorter than in a related *remote* isoquinolylidene complex of palladium [2.5198(5) Å] [29], indicating a relative weak *trans*-influence exercised by the new ligands. No significant intermolecular interactions are present in the solids of **1a** and **3b**.

2.4. Preliminary catalytic results

For purposes of comparison, Suzuki–Miyaura coupling of phenyl boronic acid and bromo acetophenone were studied under inert conditions in the presence of Cs_2CO_3 and Bu_4NBr using dimethylacetamide (DMAc) as solvent (Scheme 3). The three palladium compounds **1b**, **2b** and **3b** were used as precatalysts and compared to the three pyridylidene complexes [15] shown in Fig. 6 and $Pd(PPh_3)_4$. Experimentally determined time-conversion curves are shown in Fig. 7.

We have shown previously under somewhat different conditions that various pyridylidene complexes are significantly more effective as precatalysts than related imidazolylidene complexes. This trend is further supported by our results. With a catalyst loading of 0.1% in the presence of Bu_4NBr (0.4 mmol) as co-catalyst under inert conditions at 70 °C, the *normal* thiazolylidene complex, **1b**, (83% conversion) is a somewhat more effective precatalyst than both $Pd(PPh_3)_4$ and the *abnormal*(N) five-membered NHC complex, **2b** (72%). The *abnormal*(S) thiazolylidene compound, **3b** (65%), is the least active. All complexes are substantially less active than

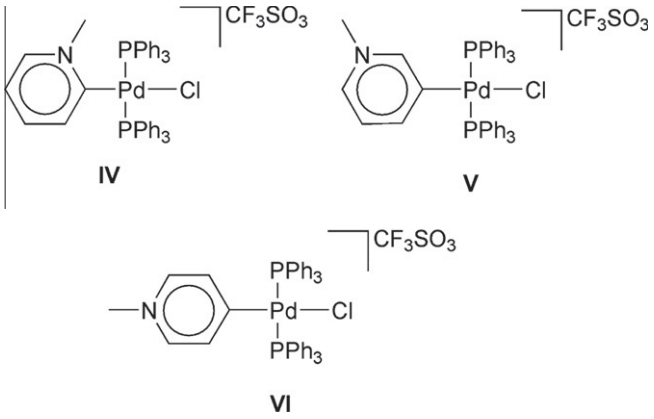


Fig. 6. Pyridylidene complexes of palladium, **IV**–**VI**.

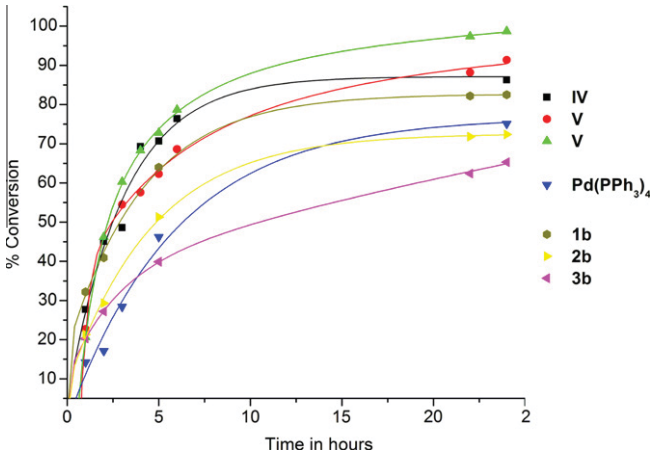


Fig. 7. Time-conversion curves for three thiazolylidene complexes of palladium in comparison with pyridylidene complexes in Suzuki–Miyaura cross-coupling. General conditions: aryl halide (2 mmol), $PhB(OH)_2$ (3 mmol), Cs_2CO_3 (4 mmol), $[Bu_4]NBr$ (0.4 mmol), catalyst (2 mmol, 0.1 mol%) in DMAc (5 ml). Yields determined by ^1H NMR spectroscopy using diethyleneglycol-di-*n*-butylether as internal standard.

Table 2
Catalytic results for Suzuki–Miyaura cross-coupling at 130 °C in air with no co-catalyst and K_2CO_3 as base; general conditions as above.

Catalyst precursor	Time (h)	Conversion (%)
IV	24	86
V	24	82
VI	25	78
1b	24	81
2b	24	82
3b	25	78

the pyridylidene complexes **IV–VI** (86–99%). At 130 °C, in air and without the co-catalyst but with K_2CO_3 as the base, the performance of the precatalysts is very similar (Table 2). Even though neither significant induction periods nor palladium black formation was observed, soluble Pd(0) colloids could still be involved while the NHC ligands maintain a certain steering and activating influence [32].

3. Conclusions

Despite the low field ^{13}C NMR chemical shifts of the carbene nucleus, particularly in *normal* 2-thiazolylidene and *abnormal* 4-thiazolylidene complexes of nickel(II) and palladium(II), their

molecular structures determined by X-ray diffraction do not support a strong carbenoic presence and point to a retention of the immonium character as in the precursor thiazolium salts. The palladium thiazolylidene complexes are weaker catalysts for Suzuki–Miyaura coupling than related pyridylidene compounds.

4. Experimental

4.1. Synthesis and characterisation

All reactions were carried out under nitrogen or argon using standard vacuum-line and Schlenk techniques. All solvents were freshly distilled under an inert atmosphere before use. THF, toluene, diethyl ether, pentane and hexane were dried over KOH or $CaCl_2$ (toluene) and distilled over sodium wire. Benzophenone and diethylene glycol dimethyl ether were used as indicators for toluene, pentane and hexane, and benzophenone for THF and diethyl ether. Dichloromethane was dried over KOH and distilled over CaH_2 [33]. $Pd(PPh_3)_4$ was prepared according to literature procedures [34].

Melting points were determined on a Stuart SMP3 apparatus and are uncorrected. Mass spectra were recorded on a AMD 604 (EI, 70 eV) or VG 70 SEQ (FAB, 70 eV, *m*-nitrobenzyl alcohol matrix) instrument, and NMR spectra on a Varian 300 FT or INOVA 600 MHz spectrometer (^{1}H NMR at 300/600 MHz, $^{13}C\{^1H\}$ NMR at 75/150 MHz and $^{31}P\{^1H\}$ NMR at 121.5/243 MHz; δ reported relative to the solvent resonance or external reference, 85% H_3PO_4). Elemental analyses were carried out at the Department of Chemistry, University of Cape Town, South Africa and the products were evacuated under high vacuum for 5 h.

4.2. Preparation of N-methyl-2-bromobenzothiazolium triflate (**I**)

The alkylating agent, methyl triflate, was added drop-wise to 2-bromothiazole (4.02 g, 24.5 mmol) in 20 ml of CH_2Cl_2 and stirred at room temperature for 17 h. The solvent was removed via a cannula and the resulting off-white precipitate was washed with THF (1× 10 ml) and diethyl ether (2× 10 ml) to yield 7.96 g (24.3 mmol) of **I**. Yield: 99.0%. Mp 241–243 °C. EI-MS, *m*/*z* (relative intensity) for $C_5H_5NO_3S_2BrF_3$: 180.0 [M^+–CF_3SO_3, 100 (^{81}Br)], 178.0 [M^+–CF_3SO_3, 98 (^{79}Br)]. ^{1}H NMR (CD_2Cl_2, δ): 8.43 (d, 1H, ^3J = 4.3 Hz, NCH), 8.23 (d, 1H, ^3J = 4.3 Hz, SCH), 4.28 (s, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 163.0 (s, C^2), 140.6 (s, NCH), 127.3 (s, SCH), 43.1 (s, NMe). *Anal.* Calc. for $C_5H_5NO_3S_2BrF_3$ (328.12): C, 18.30; H, 1.54; N, 4.27. Found: C, 17.93; H, 1.42; N, 4.13%.

4.3. Preparation of N-methyl-4-bromothiazolium triflate (**II**)

The same procedure as described for **I** was used to prepare **II** from 0.677 g (4.13 mmol) 4-bromothiazole and 0.745 g (0.514 ml, 4.54 mmol) methyl triflate to yield 1.30 g (3.96 mmol) of colourless **II**. Yield: 95.9%. Mp 145–148 °C. EI-MS, *m*/*z* (relative intensity) for $C_5H_5NO_3S_2BrF_3$: 180.0 [M^+–CF_3SO_3, 100 (^{81}Br)], 178.0 [M^+–CF_3SO_3, 98 (^{79}Br)]. ^{1}H NMR (CD_2Cl_2, δ): 10.51 (d, 1H, ^4J = 2.5 Hz, NCHS), 8.06 (d, 1H, ^4J = 2.5 Hz, SCH), 4.30 (s, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 162.5 (bs, NCS), 125.1 (s, NCBr), 121.4 (s, SCC), 43.3 (s, NMe). *Anal.* Calc. for $C_5H_5NO_3S_2BrF_3$ (328.12): C, 18.30; H, 1.74; N, 4.27. Found: C, 17.92; H, 1.80; N, 4.35%.

4.4. Preparation of N-methyl-5-bromothiazolium triflate (**III**)

The same procedure as described for **I** was used to prepare **III** from 0.585 g (3.57 mmol) 5-bromothiazole and 0.644 g (0.44 ml, 3.92 mmol) methyl triflate to yield 1.14 g (3.47 mmol) of off-white **III**. Yield: 97.3%. Mp 78.1–82.2 °C. EI-MS, *m*/*z* (relative intensity) for $C_5H_5NO_3S_2BrF_3$: 180.0 [M^+–CF_3SO_3, 100 (^{81}Br)], 178.0 [M^+–CF_3SO_3, 98 (^{79}Br)]. ^{1}H NMR (CD_2Cl_2, δ): 10.20 (s, 1H, NCHS), 8.18 (s, 1H, NCHC), 4.33 (s, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 162.1 (s, NCS), 139.0 (s, NCC), 115.8 (s, SCC), 43.6 (s, NMe). *Anal.* Calc. for $C_5H_5NO_3S_2BrF_3$ (328.12): C, 18.30; H, 1.54; N, 4.27. Found: C, 18.81; H, 1.67; N, 4.11%.

4.5. Preparation of trans-bromo(N-methyl-2,3-dihydro-thiazol-2-ylidene)bis(triphenylphosphine)-nickel(II) triflate (**1a**)

A suspension of $Ni(PPh_3)_4$ (0.667 g, 0.602 mmol) and **I** (0.195 g, 0.596 mmol) in 20 ml THF was stirred for 18 h at room temperature. The yellow precipitate in a brownish solution was filtered through Celite and washed with 2× 10 ml of toluene and 1× 5 ml of THF. The yellow product was washed through the filter with CH_2Cl_2 to yield, after solvent evaporation, 0.197 g (0.216 mmol) of complex **1a**. Yellow plates of complex **1a** were obtained via vapour diffusion of *n*-pentane into a CH_2Cl_2 solution of the product at −22 °C. Yield: 36.3%. Mp 150.0 °C (decomp.). FAB-MS, *m*/*z* (relative intensity) for $C_{41}H_{35}NO_3P_2S_2BrF_3Ni$: 761.9 [$M^+$–$CF_3SO_3$, 15 (^{81}Br, ^{58}Ni)], 499.9 [M^+–PPh_3–CF_3SO_3, 43 (^{58}Ni)], 419.0 [M^+–PPh_3–Br–CF_3SO_3, 21 (^{81}Br, ^{58}Ni)]. ^{1}H NMR (CD_2Cl_2, δ): 7.64 (m, 12H, Ph), 7.54 (m, 6H, Ph), 7.45 (m, 12H, Ph), 7.26 (d, 1H, ^3J = 3.4 Hz, NCH), 7.21 (d, 1H, ^3J = 3.4 Hz, SCH), 3.58 (s, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 200.9 (t, $^2J_{PC}$ = 32.2 Hz, NCS), 139.7 (bs, NCC), 134.4 (m, *ortho*-Ph), 131.9 (s, *para*-Ph), 129.2 (m, *ipso*- and *meta*-Ph), 125.2 (s, SCC) 43.8 (s, NMe). ^{31}P NMR (CD_2Cl_2, δ): 22.3 (s, PPh_3). *Anal.* Calc. for $C_{41}H_{35}NO_3P_2S_2BrF_3Ni$ (911.39): C, 54.03; H, 3.87; N, 1.54. Found: C, 53.79; H, 3.98; N, 1.63%.

4.6. Preparation of trans-bromo[N-methyl-2,3-dihydro-thiazol-2-ylidene)bis(triphenylphosphine)-palladium(II) triflate (**1b**)

$Pd(PPh_3)_4$ (0.781 g, 0.676 mmol) and the thiazolium salt **I** (0.219 g, 0.669 mmol) were suspended in THF (20 ml) and the mixture was stirred at room temperature for 16 h. The resulting precipitate was filtered through Celite and washed with 3× 5 ml toluene. The off-white product was washed from the filter with CH_2Cl_2 and dried under high vacuum. The resulting product had a pinkish colour which was removed by crystallising the product from CH_2Cl_2 layered with pentane at −20 °C to yield 0.0500 g (0.0520 mmol) of complex **1b**. The use of toluene as solvent and heating the mixture resulted in a brown residue which did not contain **1b**. Yield: 7.8%. Mp 225 °C (decomp.). FAB-MS, *m*/*z* (relative intensity) for $C_{41}H_{35}NO_3P_2S_2BrF_3Pd$: 733.0 [$M^+$–Br–$CF_3SO_3$, 10, (^{81}Br, ^{106}Pd)], 630.1 [$Pd(PPh_3)_2$, 6], 471.0 (M–PPh_3–Ph+H–CF_3SO_3, 25). ^{1}H NMR (CD_2Cl_2, δ): 7.57 (m, 19H, NCHC, Ph), 7.45 (m, 12H, Ph), 7.29 (d, 1H, ^3J = 3.8 Hz, SCHC), 3.55 (s, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 197.8 (s, NCS), 169.1 (s, NCC), 138.8 (s, SCC), 134.7 (bs, *ortho*-Ph), 132.3 (s, *para*-Ph), 129.5 (bs, *ipso*- and *meta*-Ph), 44.1 (s, NMe). ^{31}P NMR (CD_2Cl_2, δ): 22.6 (s, PPh_3). *Anal.* Calc. for $C_{41}H_{35}NO_3P_2S_2BrF_3Pd$ (959.12): C, 51.34; H, 3.68; N, 1.40. Found: C, 51.62; H, 3.51; N, 1.30%.

4.7. Preparation of trans-bromo[N-methyl-3,4-dihydro-thiazol-4-ylidene]bis(triphenylphosphine)-nickel(II) triflate (**2a**)

The same procedure as described for **1a** was used to prepare **2a** from **II** (0.162 g, 0.495 mmol) and $Ni(PPh_3)_4$ (0.576 g, 0.520 mmol) to yield 0.207 g (0.227 mmol) of colourless **2a**. Yield: 45.9%. Mp 172 °C (decomp.). FAB-MS, *m*/*z* (relative intensity) for $C_{41}H_{35}NO_3P_2S_2BrF_3Ni$: 762.3 [$M^+$–$CF_3SO_3$, 10 (^{81}Br, ^{58}Ni)], 500.0 (M–PPh_3–CF_3SO_3, 75), 419.1 (M–Br–PPh_3–CF_3SO_3, 33). ^{1}H NMR (CD_2Cl_2, δ): 9.22 (d, 1H, ^4J = 2.3 Hz, NCHS), 7.64 (m, 12H, Ph), 7.53 (m, 6H, Ph), 7.43 (m, 12H, Ph), 6.69 (m, 1H, SCHC), 3.92 (bs, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 163.6 (t, $^2J_{PC}$ = 35.4 Hz, NCNi), 157.8 (s, NCS), 134.6 (t, $^2J_{PC}$ = 5.7 Hz, *ortho*-Ph), 131.7 (s, *para*-Ph), 130.5 (t, $^1J_{PC}$ = 24.0 Hz, *ipso*-Ph), 129.3 (t, $^3J_{PC}$ = 5.0 Hz, *meta*-Ph), 119.7 (bs,

Table 3
Crystal data, data collection and structure refinement details of **1a**, **2b** and **3b**.

	1a·CH_2Cl_2	**2b**	**3b**·CH_2Cl_2
Formula	$C_{40}H_{35}BrNNiP_2S·CF_3O_3S·CH_2Cl_2$	$C_{40}H_{35}BrNPdP_2S·CF_3O_3S$	$C_{40}H_{35}BrNPdP_2S·CF_3O_3S·CH_2Cl_2$
M_r	996.31	959.08	1044.00
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*Pbca*
Unit cell dimensions			
a (Å)	11.4860(10)	16.007(2)	18.268(17)
b (Å)	20.7907(18)	20.895(3)	20.5765(19)
c (Å)	17.9981(15)	22.001(3)	22.679(2)
α (°)	90	90	90
β (°)	94.595(2)	96.256(3)	90
γ (°)	90	90	90
V (Å^3)	4284.2(6)	7959.6(19)	8524.8(14)
Z	4	8	8
F(000)	2024	3856	4192
μ(Mo Kα) (mm^{-1})	1.735	1.710	1.725
T (K)	100	100	100
Reflections measured	22 972	42 189	44 082
Reflections unique	7780 [R_{int} = 0.036]	14 517 [R_{int} = 0.076]	7757 [R_{int} = 0.064]
Refined parameters/restraints	515/0	975/19	515/0
R_1 [$I \geqslant 2\sigma(I)$]	0.074	0.062	0.044
wR_2[a]	0.187	0.160	0.099
Weighting scheme[a]	*a* = 0.0761	*a* = 0.0721	*a* = 0.0412
	b = 42.869	*b* = 7.8744	*b* = 13.7242
σ_{fin}(max/min) (e Å^{-3})	3.55/−2.48	2.16/−1.42	1.34/−1.50

[a] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3$.

SCC), 44.0 (s, NMe). ^{31}P NMR (CD_2Cl_2, δ): 21.6 (s, PPh_3). *Anal.* Calc. for $C_{41}H_{35}NO_3P_2S_2BrF_3Ni$ (911.39): C, 54.03; H, 3.87; N, 1.54. Found: C, 53.88; H, 3.98; N, 1.71%.

*4.8. Preparation of trans-bromo[N-methyl-3,4-dihydro-thiazol-4-ylidene]bis(triphenylphosphine)-palladium(II) triflate (**2b**)*

Compound **II** (0.105 g, 0.320 mmol) and $Pd(PPh_3)_4$ (0.37 g, 0.320 mmol) were suspended in 20 ml of toluene and stirred for 17 h at 60 °C. The colourless precipitate in a light yellow solution was allowed to cool to room temperature and filtered through Celite. The solid on the filter was washed with 2× 5 ml of toluene and the product was dissolved in CH_2Cl_2 and filtered, to yield after solvent evaporation *in vacuo* 0.287 g (0.299 mmol) of complex **2b**. Colourless needles were obtained by the vapour diffusion of *n*-pentane into a concentrated CH_2Cl_2 solution of the product. Yield: 93.5%. Mp 239 °C (decomp.). FAB-MS, *m*/*z* (relative intensity) for $C_{41}H_{35}NO_3P_2S_2BrF_3Pd$: 810.2 [$M^+$–$CF_3SO_3$, 15 (^{81}Br, ^{106}Pd)], 548.0 (M–PPh_3–CF_3SO_3, 19), 466.1 (M–Br–PPh_3–CF_3SO_3, 6). ^{1}H NMR (CD_2Cl_2, δ): 9.33 (dd, 1H, ^4J = 2.5 Hz, $^5J_{HP}$ = 0.6 Hz, NCHS), 7.54 (m, 18H, Ph), 7.42 (m, 12H, Ph), 6.52 (m, 1H, SCHC), 3.72 (bs, 3H, NMe). ^{13}C NMR (CD_2Cl_2, δ): 165.1 (t, $^2J_{PC}$ = 9.1 Hz, NCPd), 156.6 (s, NCS), 134.4 (t, $^2J_{PC}$ = 6.5 Hz, *ortho*-Ph), 131.7 (s, *para*-Ph), 129.6 (t, $^1J_{PC}$ = 24.9 Hz, *ipso*-Ph), 129.2 (t, $^3J_{PC}$ = 5.2 Hz, *meta*-Ph), 120.3 (t, $^4J_{PC}$ = 5.2 Hz, SCC), 44.2 (s, NMe). ^{31}P NMR (CD_2Cl_2, δ): 22.6 (s, PPh_3). *Anal.* Calc. for $C_{41}H_{35}NO_3P_2S_2BrF_3Pd$ (959.12): C, 51.34; H, 3.68; N, 1.46. Found: C, 51.02; H, 3.71; N, 1.54%.

*4.9. Preparation of trans-bromo[N-methyl-3,5-dihydro-thiazol-5-ylidene]bis(triphenylphosphine)-palladium(II) triflate (**3b**)*

The same procedure as described for **2b** was used to prepare **3b** from $Pd(PPh_3)_4$ (0.191 g, 0.165 mmol) and the triflate salt **III** (0.054 g, 0.165 mmol) to obtain 0.138 g (0.144 mmol) of the off-white product. Yield: 87.2%. Mp 189 °C (decomp.). FAB-MS, *m*/*z* (relative intensity) for $C_{41}H_{35}NO_3P_2S_2BrF_3Pd$: 810.3 [$M^+$–$CF_3SO_3$, 16 (^{81}Br, ^{106}Pd)], 548.1 (M–PPh_3–CF_3SO_3, 14), 466.1 (M–Br–PPh_3–CF_3SO_3, 6). ^{1}H NMR (CD_2Cl_2, δ): 9.28 (m, 1H, NCHS), 7.56 (m, 12H, Ph), 7.51 (m, 6H, Ph), 7.41 (m, 12H, Ph), 6.30 (m, 1H, NCHC), 3.59 (d, 3H, ^4J = 0.6 Hz, NMe). ^{13}C NMR (CD_2Cl_2, δ): 158.7 (bs, NCS), 154.3 (s, NCC), 135.7 (t, $^2J_{PC}$ = 4.3 Hz, CPd), 134.8 (t, $^2J_{PC}$ = 6.1 Hz, *ortho*-Ph), 131.6 (s, *para*-Ph), 129.6 (t, $^1J_{PC}$ = 25.4 Hz, *ipso*-Ph), 128.8 (t, $^3J_{PC}$ = 5.2 Hz, *meta*-Ph), 41.0 (s, NMe). ^{31}P NMR (CD_2Cl_2, δ): 24.3 (s, PPh_3). *Anal.* Calc. for $C_{41}H_{35}NO_3P_2S_2BrF_3Pd$ (959.12): C, 51.34; H, 3.68; N, 1.46. Found: C, 51.68; H, 3.52; N, 1.53%.

4.10. Representative procedure for the Suzuki–Miyaura coupling

Phenylboronic acid (3 mmol, 0.366 g), bromo acetophenone (2 mmol, 0.398 g), potassium carbonate/cesium carbonate (4 mmol, 0.553/1.30 g), Bu_4NBr (0.4 mmol, 0.129 g), diethyleneglycol-di-*n*-butylether (2 mmol, 0.437 g) and dimethylacetamide (5 ml) were placed in a 25 ml two-neck round bottomed flask. The flask was equipped with a reflux condenser and a septum and placed into an oil bath pre-heated to 70 or 130 °C. The catalyst solution was added after thermostating for 5 min. Aliquots (0.2 ml) were removed at regular intervals from the reaction mixture and added to CH_2Cl_2 (5 ml). The organic layer was washed with H_2O (3× 5 ml), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was analysed by ^{1}H NMR spectroscopy.

For inert conditions, the dry chemicals were placed in a three-neck round bottomed flask (equipped with a reflux condenser) that was evacuated and flushed with N_2. Degassed dimethylacetamide and diethyleneglycol-di-*n*-butylether were added under a positive stream of N_2. The condenser and the open neck on the round bottomed flask were equipped with septa. The nitrogen atmosphere was maintained by a balloon filled with nitrogen that was connected through the septa on the condenser via a needle. The catalyst solution was added after thermostating for 5 min. Aliquots (0.2 ml) were taken at regular intervals and treated as described above.

4.11. Crystal structure determinations

Data associated with the crystal structures are summarised in Table 3. Intensity data were collected at *T* = 100 K with a Bruker SMART Apex diffractometer with graphite-monochromated Mo

Kα radiation (λ = 0.71073 Å). Intensities were measured using the ω-scan mode and were corrected for Lorentz and polarisation effects [35–38]. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 (SHELXL-97) [39]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealised positions and refined using a riding model with fixed isotropic contributions. Crystals of **1a** and **3b** contained one molecule of CH_2Cl_2 each. These solvent molecules as well as the triflate counter ions in all structures showed signs of disorder, which could however not be resolved resulting in large displacement parameters of the respective atoms which is also reflected in the *R* values. In order to stabilise refinement, the triflate molecules in **2b** were restrained to a similar geometry by using the SAME instruction within the SHELXL-97 software package.

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Appendix A. Supplementary data

CCDC 821852, 821853 and 821854 contain the supplementary crystallographic data for **1a**, **2b**, and **3b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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